NASA Technical Memorandum 89152

ADHESIVE EVALUATION OF WATER-SOLUBLE LARC-TPI

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(NASA-TM-89152) ADHESIVE EVALUATION OF WATER-SOLUBLE LARC-TPI (NASA) 29 p Avail: NTIS HC A03/MF A01 CSCL 11A
N87-23752
Unclas
H1/27 0080165

JUNE 1987

National Aeronautics and
Space Administration

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INTRODUCTION

A linear thermoplastic polyimide, LARC-TPI, was developed several years ago at NASA Langley Research Center (LaRC) which showed promise as a high temperature adhesive for applications in aircraft and spacecraft. The material was of interest because of its toughness, flexibility, good thermal and thermooxidative stability and other desirable properties.[1-6] The material had been investigated by Boeing Aircraft Company as a high temperature adhesive for bonding titanium adherends and found to retain its high strength for 37000 hours at 232°C.[7,8]

A water soluble version of the LARC-TPI, identified as TPI(MTC)/H2O in this paper, was synthesized at United Technologies Research Center, East Hartford, Connecticut from a polyamic-acid solution in diglyme prepared by Mitsui Toatsu Chemicals, Incorporated (MTCI), Tokyo, Japan. A water solvent used in the manufacturing and processing of an adhesive is very attractive because present polyimide adhesives, as well as matrix resins, use organic solvents which are relatively expensive and require strict safety and environmental requirements during manufacture and processing.

MTCI was licensed by the U.S. Government in March 1984 to produce the LARC-TPI for subsequent sale in the U.S. MTCI made it commercially available the latter part of 1984 and it is presently available as a solution, film, and semi-crystalline powder. The polyamic-acid solution manufactured by MTCI is identified as TPI/MTC in this paper. The materials, a polyamic-acid solution and a water-soluble solution, were prepared as adhesive tapes and used to bond titanium adherends.

This report details the results of a study (1) on the adhesive bond strength of TPI(MTC)/H2O up to 232°C for two bonding pressures (2) on the effects of thermal exposure for 500, 1000 and 5000 hrs at 204°C and a 72-hour water-boil on the lap shear strength for TPI(MTC)/H2O adhesive. These test results are compared with data previously reported for TPI/MTC.[9]

EXPERIMENTAL

<u>Materials</u>. A water-soluble polyamic-carboxylate solution, identified as TPI(MTC)/H2O in this report, was prepared at United Technologies Research Center (UTRC), East Hartford, Connecticut.[10] The material was prepared as the quaternary N,N-dimethylethanol amine salt according to the following procedure. The 30% solids solution in diglyme of TPI/MTC (100 g) was diluted with 90 ml of diglyme and 10 ml of ethyl alcohol to give a 15% solids solution. The resulting solution was injected under pressure through a 25-30 mil diameter nozzle into 3000 ml of rapidly stirred distilled water (Ross mixer) over a 7-10 minute time period. The finely divided resin powder was collected by filtration, washed well with 2000 ml distilled water and vacuum dried at 50°C for 20 hours. The fine white powder had an acid number of 194.5.

Small scale batches of the TPI(MTC)/H2O were made by dissolving 10 g of dry powder in a solution of 4 g of dimethylethanol amine and 95 ml of distilled water with stirring at 50-60°C. The resulting clear amber 9.7% solids solution had a viscosity of 7 cs at 25°C. The viscosity of TPI(MTC)/H2O was found to increase rapidly above this concentration as illustrated in Figure 1. For this reason, the 9.7% solids solution was used in this study. The resin solution was used for preparing the adhesive tape as well as for use as a primer.

A 29.1 wt % solids polyamic-acid solution in bis(2-methoxyethyl)ether (diglyme) was manufactured and supplied by Mitsui Toatsu Chemicals, Incorporated (MTCI), Tokyo, Japan. The monomers used in the preparation of LARC-TPI were 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) and 3,3'-diaminobenzophenone (3,3'-DABP).[2,7] The polyamic-acid solution supplied by MTCI is identified as TPI/MTC in this report. The solution, lot no. 26-001, had an η_{inh} of 0.54 dl/g (35°C) and a Brookfield viscosity of 24,600 cps (23°C).

Characterization. Lap shear strength (LSS) was obtained according to ASTM D-1002 using a Model TT Instron universal testing machine. The average LSS's reported represent at least four lap shear specimens tested for any one condition except as noted in the tables. Elevated temperature tests were conducted in a clam-shell, quartz-lamp oven with temperature controlled to within ± 3°C for all tests. Specimens were held 10 min at temperature prior to testing except for the water-boil specimens which were tested as soon as the test temperature was reached. The range of LSS's is indicated by dashed lines in the bar graph figures and given in the tables.

Bondline thickness was obtained as the difference between the total joint thickness measured with a micrometer and the sum of the adherend thicknesses. The average bondline thickness was 0.086 mm (0.0039 in.) for TPI(MTC)/H2O and 0.091 mm (0.0036 in.) for TPI/MTC.

Glass transition temperatures (Tg) of the adhesive from the fractured lap shear specimens were determined by thermomechanical analysis (TMA) on a DuPont 943 Analyzer in static air at a heating rate of 5°C/min using a hemispherical probe with a 15 g mass.

Inherent viscosity (η_{inh}) was determined using a Cannon-Ubbelohde viscometer in a 35°C water bath controlled to within ± 0.01°C. A 10 ml solution of 0.5% solids in N,N-dimethylacetamide (DMAC) was made and filtered. The average of three runs of the solution was reported.

Adhesive Tape. Adhesive tape for the TPI/MTC was prepared by brush coating a 7.5 wt % solids polyamic-acid primer solution in diglyme onto 0.01 cm thick 112 E-glass cloth with A-1100 finish (γ-aminopropylsilane). The glass cloth served as a carrier for the adhesive as well as for bondline control and as an escape channel for solvent and volatile reaction products. After the primer was applied, the coating was air-dried for 1 hr and heated in a forced air oven for 1 hr at each of three temperatures: 100°C, 150°C, and 175°C. Due to the difficulty of applying the as-supplied 29.1 wt % solids solution, it was necessary to dilute the solution to approximately 24 wt % solids for easier brush application onto the glass cloth. Subsequent applications were exposed to the following schedule until a thickness of 0.02 - 0.025 cm was obtained:

(1) Room temperature for 1 hr

(2) RT → 100°C, hold 1 hr

(3) 100°C → 150°C, hold 2 hrs

(4) 150°C → 175°C, hold 3 hrs

The rather involved procedure to prepare the tape was necessary to drive off solvent and reaction product volatiles when converting the polyamic-acid resin to the polyimide. Imidization of polyamic-acids to polyimides generally occurs above 160°C with the degree of conversion being a function of time at temperature.

Adhesive tape for the TPI(MTC)/H20 was prepared in a similar manner using a 9.7 wt % solids solution in water containing the N,N-dimethylethanol amine salt prepared at UTRC. This water soluble polyamic-carboxylate undergoes thermal conversion to the polyimide just as in the case of the polyamic-acid. After applying the 9.7 wt % solids solution on the glass cloth, the resin was air-dried for 0.5 hr with subsequent heating for 0.5 hr at each of the three temperatures, 100°C, 150°C, 175°C, until a tape thickness of 0.025 cm was obtained. Diffuse Reflectance-Fourier Transform Infrared (DR-FTIR) spectra were obtained on a similar solution which showed imide formation after a single cycle (i.e., air-dry, 0.5 hr; 100°C, 0.5 hr; 150°C, 0.5 hr) and reported in reference 9.

Adhesive Bonding. The prepared adhesive tapes were used to bond titanium adherends (Ti 6Al-4V, per Mil-T-9046E, Type III Comp.) with a nominal thickness of 0.13 cm. The four-fingered Ti(6Al-4V) panels were grit blasted with 120 grit aluminum oxide, washed with methanol, and treated with a Pasa-Jell 107* treatment to form a stable oxide on the surface. The adherends were washed with water and dried in a forced-air oven at 100°C for 5 min. The treated adherends were primed within two hours of the surface treatment by applying a thin coat of the respective adhesive solutions on the surfaces to be bonded. They were air-dried under a fume hood for 0.5 hr then placed in a forced-air oven and heated for 15 to 30 min at 100°C and 15 to 30 min at 150°C. The primed adherends were stored in a polyethylene bag

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*Trade name for a titanium surface treatment available from Semco, Glendale, CA.

and placed in a desiccator until needed. Lap shear specimens were prepared by inserting the adhesive tape between the primed adherends using a 1.27 cm overlap (ASTM D-1002) and applying pressure in a hydraulic press. The bonding cycles used during this study were as follows:

Cycle 1

(1) Apply 0.34 MPa pressure, heating rate ≈ 8°C/min, RT → 343°C, hold 1 hr

(2) Cooled under pressure to ≈ 150°C and removed from bonding press

Cycle 2

(1) Apply 2.07 MPa pressure, heating rate ≈ 8°C/min, RT → 343°C, hold 1 hr

(2) Cool under pressure to ≈ 150°C and remove from bonding press

Thermal and Water-boil Exposure. TPI(MTC)/H20 lap shear specimens were thermally exposed in a forced-air oven for 500, 1000, and 5000 hrs at 204°C. The forced-air oven was controlled to within ± 1% of the exposure temperature. Lap shear strength tests were conducted at RT, 177°C, 204°C, and 232°C before (controls) and after exposure.

A rather severe 72-hour water-boil test was conducted in laboratory glassware containing boiling distilled water. Lap shear specimens were immersed (above the bonded area) during the 72-hour period. Lap shear strengths were determined at RT, 177°C, 204°C, and 232°C.

RESULTS AND DISCUSSION

Materials and Chemistry. The proposed reactions for the formation of the subject thermoplastic polyimides are shown in Figure 2. The monomers used in the preparation were BTDA and 3,3'-DABP. The water-soluble polyamic-carboxylate (I) [TPI(MTC)/H20] undergoes a thermal conversion with elimination of water and N,N-dimethylethanol amine to form the polyimide (III), whereas in the other scheme, the polyamic-acid (II) eliminates water to form the polyimide.

Imide formation was shown in reference 9 during preparation of an adhesive tape and on a fractured lap shear specimen for LARC-TPI prepared from a water soluble material similar to the TPI(MTC)/H20 used in the present study.

TPI(MTC)/H20 Bonding Pressure. The prepared TPI(MTC)/H20 adhesive tape was used to bond titanium with a Pasa-Jell treatment which forms a stable oxide on the surface to be bonded. The two bonding cycles used for this part of the study were described earlier. Lap shear strength tests were conducted at RT, 177°C, 204°C, and 232°C (Table I and Figure 3). Results are expressed in graphical form for those interested in obtaining a quick pictorial summary of results and in tabular form for those interested in more detail and additional information not included in the graphs such as Tg, failure mode, and the number of specimens tested. The lap shear strengths and trends are the same for both bonding pressures used with the average strength decreasing slightly at 204°C, ≈ 90% of the RT strength, and an even greater decrease at 232°C, ≈ 69% of RT strength. All failures were primarily cohesive. The Tg is determined for those specimens tested at 232°C were significantly lower (230°C and 222°C) than those specimens tested at RT, 177°C, and 204°C (range from 240°C to 250°C). The reason for this difference is not known at this time. Because 2.07 MPa bonding pressure had been used in the earlier reported work with TPI/MTC for which comparisons are made, and because no significant difference in results for TPI(MTC)/H20 was noted for the two bonding pressures, the 2.07 MPa was used for the remainder of this evaluation for the TPI(MTC)/H20 adhesive.

Thermal Exposure. Long term thermal stability was determined by exposing unstressed lap shear specimens at 204°C for up to 5000 hrs in a forced-air oven. Lap shear strength was determined at RT, 177°C, 204°C, and 232°C before (controls) and after exposure.

Results are given in Table II and Figure 4 for TPI(MTC)/H20 which indicate no appreciable difference for the lap shear strengths at RT, 177°C, and 204°C for up to 5000 hrs exposure. The range of values is from 24.8 MPa to 27.8 MPa. However, a significant decrease in strength was found for those thermally aged up to 1000 hrs at 204°C and tested at 232°C (16.7 MPa to 19.3 MPa). On further aging to 5000 hrs at 204°C, the strength at 232°C increases to 21.9 MPa. This type of behavior is not uncommon for polyimides. These are encouraging results because the adhesive retains excellent strength for long term thermal exposure. All specimen failures were primarily cohesive -- the desirable mode of failure. The color of the adhesive was very dark, almost black. Again, the Tgs for those tested at 232°C, except for those thermally aged for 5000 hrs, were low compared to the rest of the measurements.

Data obtained from reference 9 for TPI/MTC are given in Table III and Figure 5 for lap shear strength tests performed at RT, 177°C, and 204°C. A general trend of decreasing lap shear strength with increasing test temperature was obtained for all those tested up to 1000 hrs. Those thermally exposed for 5000 hrs nominally gave the same strength for all tests (25.7 MPa to 27.1 MPa). The decrease is small, less than 24%, for specimens aged up to 1000 hrs. All failures were 100% cohesive. The adhesive was an amber color, whereas that of the TPI(MTC)/H2O was almost black. A possible trend of increasing Tg with time of thermal aging was noted.

When comparing the two adhesives, the data indicates higher strengths were obtained for the TPI/MTC system. The TPI(MTC)/H2O strengths obtained for up to 204°C tests ranged from 80% to 100% of the TPI/MTC strengths with only two values less than 91%. Obviously, both systems retain excellent strengths at test temperatures up to 204°C for at least 5000 hrs. Earlier mention was given to the fact that Boeing Aircraft Company had found excellent strength retention for up to 37,000 hrs (chromic acid anodized titanium adherends).[8] Considering the advantages of a water-soluble system, the TPI(MTC)/H2O performed exceptionally well during long term thermal exposure.

72-Hour Water-boil. Results of the 72-hour water-boil test for lap shear specimens bonded with TPI(MTC)/H2O adhesive are given in Table IV and shown in Figure 6. Lap shear strength was determined at RT, 177°C, 204°C, and 232°C. RT lap shear strength decreased from 26.8 MPa to 23.3 MPa. The 177°C, 204°C, and 232°C lap shear strengths were, respectively, 73%, 48%, and 46% of their control strengths at those temperatures. Therefore, the effect of the 72-hour water-boil was to significantly reduce the strength of the bonded joint. All failures were cohesive. No obvious trend was noted for the measured Tgs except that, again, the Tgs measured at 232°C were lower than the rest with no apparent reason for this occurrence.

Results of the 72-hour water-boil test for lap shear specimens bonded with TPI/MTC adhesive taken from reference 9 are given in Table V and

Figure 7. LSS was determined at RT, 177°C, ad 204°C. No tests were performed at 232°C. RT lap shear strength decreased 16% from 33.0 MPa to 27.8 MPa. Significant lap shear strength decreases were obtained at 177°C and 204°C which were only 66% and 40% respectively those of the controls' strengths. All failures were 100% cohesive. Tgs are also given in the last column of Table V and for the water-boil specimens indicate a possible trend of decreasing Tg with increasing test temperature. Because only single measurements were made and because of the measurement technique, the trend is inconclusive.

The two adhesive systems, TPI(MTC)/H2O and TPI/MTC, react essentially the same to the water-boil exposure. The lap shear strengths were significantly reduced from those of the control strengths. Both systems failed cohesively and had Tgs that fell in approximately the same range for test temperatures up to 204°C [221°C to 245°C for TPI(MTC)/H2O and 225°C to 239°C for TPI/MTC].

Comparison with Literature Data for TPI Adhesives. Comparisons with literature data (Table VI) for LARC-TPI adhesives were made for the common test temperatures of RT and 232°C. The material identified as TPI/H2O in reference 9 was prepared in a similar manner to that in the present study for the TPI(MTC)/H2O. The TPI/H2O was prepared at UTRC from LARC-TPI/ diglyme solution synthesized at LaRC whereas the present material (LARC-TPI) was obtained from a commercial source, MTCI. Although a slight difference is noted in the bonding conditions, the lap shear strength results of the two materials compare very favorably, i.e., RT strengths of 26.8 MPa and 30.3 MPa, 232°C strengths of 19.3 MPa and 17.4 MPa. Comparisons of TPI(MTC)/H2O with data of adhesives not prepared in water are similar for those of references 7 and 9 but are significantly lower than those of reference 1 for the RT strength, 26.8 MPa versus 41.4 MPa. Other factors influencing strengths may involve variations in surface preparations, bonding conditions and the starting resin solutions. The material of the present study, TPI(MTC)/H2O, compares overall very favorably with that reported in the literature and shows promise as a water-soluble adhesive for use in various applications.

SUMMARY

A water-soluble version of LARC-TPI prepared by United Technologies Research Center, East Hartford, Connecticut, from the commercial product marketed by Mitsui Toatsu Chemicals, Incorporated, Tokyo, Japan was evaluated as a thermoplastic adhesive for bonding titanium alloy, Ti-6Al-4V. LARC-TPI polymer, synthesized in diglyme, has shown promise as a high temperature thermoplastic adhesive for potential applications in aircraft and spacecraft. The polymer has excellent high temperature properties such as good thermal and thermooxidative stability as well as good toughness and flexibility. A water-soluble version of the polymer is very attractive because of low cost and the strict environmental safety requirements associated with organic solvents.

The water-soluble version, identified as TPI(MTC)/H2O, was prepared as an adhesive tape and used to bond Ti-6Al-4V adherends. Lap shear strength was the primary mechanical test performed to evaluate the adhesive before (controls) and after thermal aging in air up to 5000 hrs at 204°C and after a 72-hour water-boil exposure. Lap shear strength tests were conducted at

RT, 177°C, 204°C, and 232°C. The adhesive was characterized after fracture by determining the Tg (by TMA measurement) as well as defining the mode of fracture, either cohesive or adhesive, by visual observation.

A detailed comparison of the TPI(MTC)/H2O was made with the adhesive identified as TPI/MTC, a polyamic-acid prepared in diglyme, reported in reference 9 (work also performed by this laboratory). A limited comparison was also made with other literature data for LARC-TPI.

The effect of bonding pressures, 0.34 MPa and 2.07 MPa, during the bonding process was determined with the results indicating no appreciable differences in the bond strengths. A general decrease in lap shear strength with test temperatures was shown for 204°C and 232°C, approximately 90% and 69% of the RT strength, respectively.

Long term thermal exposure at 204°C of unstressed TPI(MTC)/H2O bonded lap shear specimens in a forced-air oven for up to 5000 hrs indicated no appreciable change in the lap shear strengths at RT, 177°C, and 204°C. A decrease in strength for the 232°C test temperature was observed for up to 1000 hrs which then increased significantly for those exposed for 5000 hrs. The lap shear strengths were very high for all the RT, 177°C, and 204°C tests [ranged from 24.8 MPa (3600 psi) to 27.8 MPa (4040 psi)] and they still had good strength, 16.7 MPa (2420 psi) to 21.9 MPa (3180 psi), for the 232°C tests. All failures were cohesive. The Tgs ranged from a low of 222°C to a high of 251°C.

A 72-hour water-boil test of the TPI(MTC)/H2O lap shear specimens resulted in a significant reduction in the lap shear strengths. The RT, 177°C, 204°C, and 232°C lap shear strengths were, respectively, 87%, 73%, 48%, and 46% of their control strengths at those temperatures. Therefore, the effect of the water-boil exposure was to significantly reduce the strengths of the bonded joints. The measured Tgs of the water-boil specimens indicate a possible trend of decreasing Tg with increasing test temperature.

The adhesive of the present study, TPI(MTC)/H2O, was determined to compare very favorably with other versions reported in literature and, therefore, shows promise as a water-soluble adhesive for use in various applications.

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TABLE I. - EFFECT OF BONDING PRESSURE ON LSS OF TPI(MTC)/H2O ADHESIVE BONDED Ti-6Al-4V

Bonding Pressure, MPa (psi)	Number of Specimens	Test Temperature, °C (°F)	Average LSS, MPa (psi)	Range of LSS, MPa (psi)	Primary Failure Mode[a]	Glass Transition Temperature, Tg[b] °C (°F)
0.34 (50)	4	RT (RT)	28.0 (4060)	27.6-28.3 (4000-4100)	Co	250 (482)
	4	177 (350)	27.8 (4030)	27.4-28.2 (3980-4090)	Co	242 (467)
	4	204 (400)	24.4 (3530)	23.6-25.6 (3420-3710)	Co	240 (464)
	4	232 (450)	18.5 (2680)	17.2-19.4 (2500-2820)	Co	230 (446)
2.07 (300)	4	RT (RT)	26.8 (3890)	25.7-28.0 (3720-4070)	Co	245 (473)
	4	177 (350)	27.8 (4040)	26.7-28.4 (3880-4120)	Co	240 (464)
	4	204 (400)	25.3 (3680)	24.5-26.1 (3550-3790)	Co	245 (473)
	3	232 (450)	19.3 (2800)	18.3-20.0 (2650-2900)	Co	222 (432)[c]

Bonding conditions: heating rate of 8°C/min (14°F/min), RT to 343°C (650°F), held 1 hr

[a] Cohesive - Co

[b] Single measurement

[c] Average of 3 specimens

TABLE II. - LSS TEST RESULTS OF THERMAL EXPOSURE AT 204°C FOR TPI(MTC)/H2O ADHESIVE BONDED Ti-6Al-4V

Time of Exposure at 204°C, hr	Number of Specimens	Test Temperature, °C (°F)	Average LSS, MPa (psi)	Range of LSS, MPa (psi)	Primary Failure Mode[a]	Glass Transition Temperature, Tg[b] °C (°F)
Controls	4	RT (RT)	26.8 (3890)	25.7-28.0 (3720-4070)	Co	245 (473)
	4	177 (350)	27.8 (4040)	26.7-28.4 (3880-4120)	Co	240 (464)
	4	204 (400)	25.3 (3680)	24.5-26.1 (3550-3790)	Co	245 (473)
	3	232 (450)	19.3 (2800)	18.3-20.0 (2650-2900)	Co	222 (432)[c]
500	4	RT (RT)	26.6 (3860)	24.4-29.2 (3540-4240)	Co	244 (471)
	4	177 (350)	26.4 (3820)	24.8-27.3 (3600-3960)	Co	246 (475)
	4	204 (400)	25.5 (3700)	24.7-26.2 (3580-3800)	Co	249 (480)
	4	232 (450)	18.5 (2690)	18.1-19.3 (2620-2800)	Co	237 (459)
1000	4	RT (RT)	26.7 (3880)	25.8-27.2 (3750-3950)	Co	242 (468)
	4	177 (350)	27.4 (3970)	27.0-27.7 (3920-4020)	Co	246 (475)
	4	204 (400)	25.4 (3680)	24.3-26.2 (3520-3800)	Co	237 (459)
	4	232 (450)	16.7 (2420)	14.8-18.6 (2140-2700)	Co	230 (446)
5000	4	RT (RT)	24.8 (3600)	24.1-25.8 (3500-3750)	Co	250 (482)
	4	177 (350)	25.9 (3760)	24.8-26.8 (3600-3890)	Co	251 (484)
	4	204 (400)	25.2 (3660)	25.0-25.6 (3630-3710)	Co	248 (478)
	4	232 (450)	21.9 (3180)	21.3-23.0 (3100-3340)	Co	248 (478)

Bonding conditions: 2.07 MPa (300 psi) pressure, heating rate of 8°C/min (14°F/min), RT to 343°C (650°F), held 1 hr

[a] Cohesive - Co

[b] Single measurement

[c] Average of 3 specimens

TABLE III. - LSS TEST RESULTS OF THERMAL EXPOSURE AT 204°C FOR TPI/MTC BONDED Ti-6Al-4V

Time of Exposure at 204°C, hr	Number of Specimens	Test Temperature, °C (°F)	Average LSS, MPa (psi)	Range of LSS, MPa (psi)	Primary Failure Mode[a]	Glass Transition Temperature, Tg[b] °C (°F)
0 (Controls)	4	RT (RT)	33.0 (4790)	32.3-33.5 (4680-4860)	Co	228 (442)
	4	177 (350)	29.5 (4280)	28.8-30.7 (4180-4450)	Co	225 (437)
	4	204 (400)	25.2 (3660)	25.0-25.4 (3620-3690)	Co	236 (457)
	8	232 (450)	17.5 (2540)	14.8-19.7 (2150-2800)	Co	225 (437)
500	4	RT (RT)	34.1 (4940)	32.7-35.3 (4740-5120)	Co	242 (468)
	4	177 (350)	29.0 (4200)	27.5-30.5 (3980-4420)	Co	242 (468)
	4	204 (400)	26.9 (3900)	26.6-27.1 (3860-3940)	Co	237 (459)
1000	4	RT (RT)	32.9 (4780)	32.3-34.4 (4690-4980)	Co	242 (468)
	4	177 (350)	29.9 (4340)	28.5-31.0 (4140-4490)	Co	246 (475)
	4	204 (400)	27.8 (4020)	27.2-28.6 (3940-4160)	Co	238 (460)
5000	4	RT (RT)	27.1 (3930)	26.0-27.4 (3760-3970)	Co	251 (484)
	4	177 (350)	25.7 (3730)	24.5-26.4 (3550-3820)	Co	247 (477)
	4	204 (400)	26.0 (3770)	24.7-26.9 (3580-3900)	Co	238 (460)

Bonding conditions: 2.07 MPa (300 psi) pressure, heating rate of 8°C/min (14°F/min), RT to 343°C (650°F), held 1 hr

[a] Cohesive - Co

[b] Single measurement

TABLE IV. - LSS TEST RESULTS OF A 72-HOUR WATER-BOIL FOR TPI(MTC)/H20 ADHESIVE BONDED Ti-6Al-4V

	Number of Specimens	Test Temperature, °C (°F)	Average LSS, MPa (psi)	Range of LSS, MPa (psi)	Primary Failure Mode[a]	Glass Transition Temperature, Tg[b] °C (°F)
Controls	4	RT (RT)	26.8 (3890)	25.7-28.0 (3720-4070)	Co	245 (473)
	4	177 (350)	27.8 (4040)	26.7-28.4 (3880-4120)	Co	240 (464)
	4	204 (400)	25.3 (3680)	24.5-26.1 (3550-3790)	Co	245 (473)
	3	232 (450)	19.3 (2800)	18.3-20.0 (2650-2900)	Co	222 (432)[c]
72-Hour Water-boil	4	RT (RT)	23.3 (3380)	21.2-26.5 (3070-3850)	Co	230 (446)
	4	177 (350)	20.4 (2960)	19.3-21.6 (2800-3130)	Co	221 (430)
	4	204 (400)	12.2 (1770)	11.8-13.1 (1720-1900)	Co	221 (430)
	4	232 (450)	8.9 (1290)	7.6-12.3 (1100-1780)	Co	216 (421)

Bonding conditions: 2.07 MPa (300 psi) pressure, heating rate of 8°C/min (14°F/min), RT to 343°C (650°F), held 1 hr

[a] Cohesive - Co

[b] Single measurement

[c] Average of 3 specimens

TABLE V. - LSS TEST RESULTS OF A 72-HOUR WATER-BOIL FOR TPI/MTC BONDED Ti-6Al-4V

	Number of Specimens	Test Temperature, °C (°F)	Average LSS, MPa (psi)	Range of LSS, MPa (psi)	Primary Failure Mode[a]	Glass Transition Temperature, T_g[b] °C (°F)
Controls	4	RT (RT)	33.0 (4790)	32.3-33.5 (4680-4860)	Co	228 (442)
	4	177 (350)	29.5 (4280)	28.8-30.7 (4180-4450)	Co	225 (437)
	4	204 (400)	25.2 (3660)	25.0-25.4 (3620-3690)	Co	236 (457)
72-Hour Water-boil	4	RT (RT)	27.8 (4030)	26.7-28.8 (3870-4180)	Co	239 (462)
	4	177 (350)	19.7 (2860)	19.1-20.3 (2760-2950)	Co	230 (446)
	4	204 (400)	10.1 (1470)	9.4-11.0 (1360-1600)	Co	225 (437)

Bonding conditions: 2.07 MPa (300 psi) pressure, heating rate of 8°C/min (14°F/min), RT to 343°C (650°F), held 1 hr

[a] Cohesive - Co
[b] Single measurement

TABLE VI. - LAP SHEAR STRENGTH COMPARISON OF TPI ADHESIVES[a]

Data Source	Surface Treatment	Bonding Conditions	Test Temperature, °C (°F)	Avg. LSS, MPa (psi)	Primary Failure Mode[b]
Present study TPI(MTC)/H2O	Pasa-Jell 107	2.07 MPa; 8°C/min, RT → 343°C, hold 343°C for 1 hr	RT (RT)	26.8 (3890)	Co
			177 (350)	27.8 (4040)	Co
			204 (400)	25.3 (3680)	Co
			232 (450)	19.3 (2800)	Co
LARC-TPI Ref. 1	Pasa-Jell 107	7°C/min, RT → 325°C, apply 1.38 MPa at 280°C; hold 5 min at 325°C	RT (RT)	41.4 (6000)	--
			232 (450)	17.9 (2600)	--
LARC-TPI Ref. 7	Chromic acid anodize (CCA)	1.38 MPa; 2-3°C/min, RT → 343°C, hold 90 min; postcure 2 hrs at 316°C	RT (RT)	29.7 (4300)	--
			232 (450)	14.8 (2150)	--
TPI/MTC Ref. 9	Pasa-Jell 107	2.07 MPa; 8°C/min, RT → 343°C, hold 343°C for 1 hr	RT (RT)	33.0 (4790)	Co
			177 (350)	29.5 (4280)	Co
			204 (400)	25.2 (3660)	Co
			232 (450)	15.8 (2280)	Co
TPI/H_2O Ref. 9	Pasa-Jell 107	1.38 MPa; 8°C/min, RT → 325°C, hold 30 min	RT (RT)	30.3 (4400)	Co
			232 (450)	17.4 (2520)	Co
			278 (532)	3.2 (460)	Ad

[a] Titanium (6AL-4V) adherends

[b] Cohesive-Co; adhesive - Ad

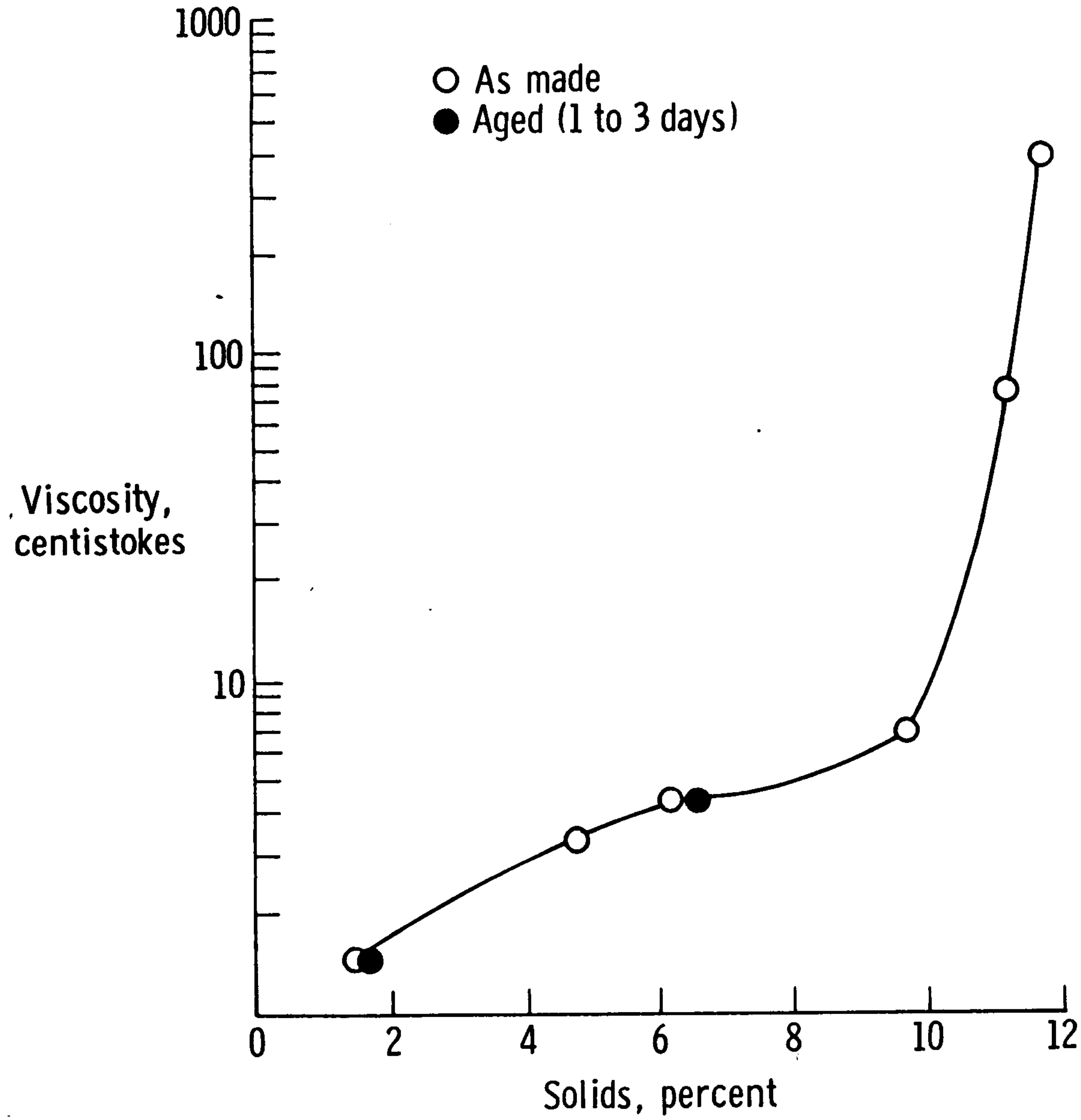

Figure 1. Viscosity of TPI(MTC)/H2O as a function of concentration.

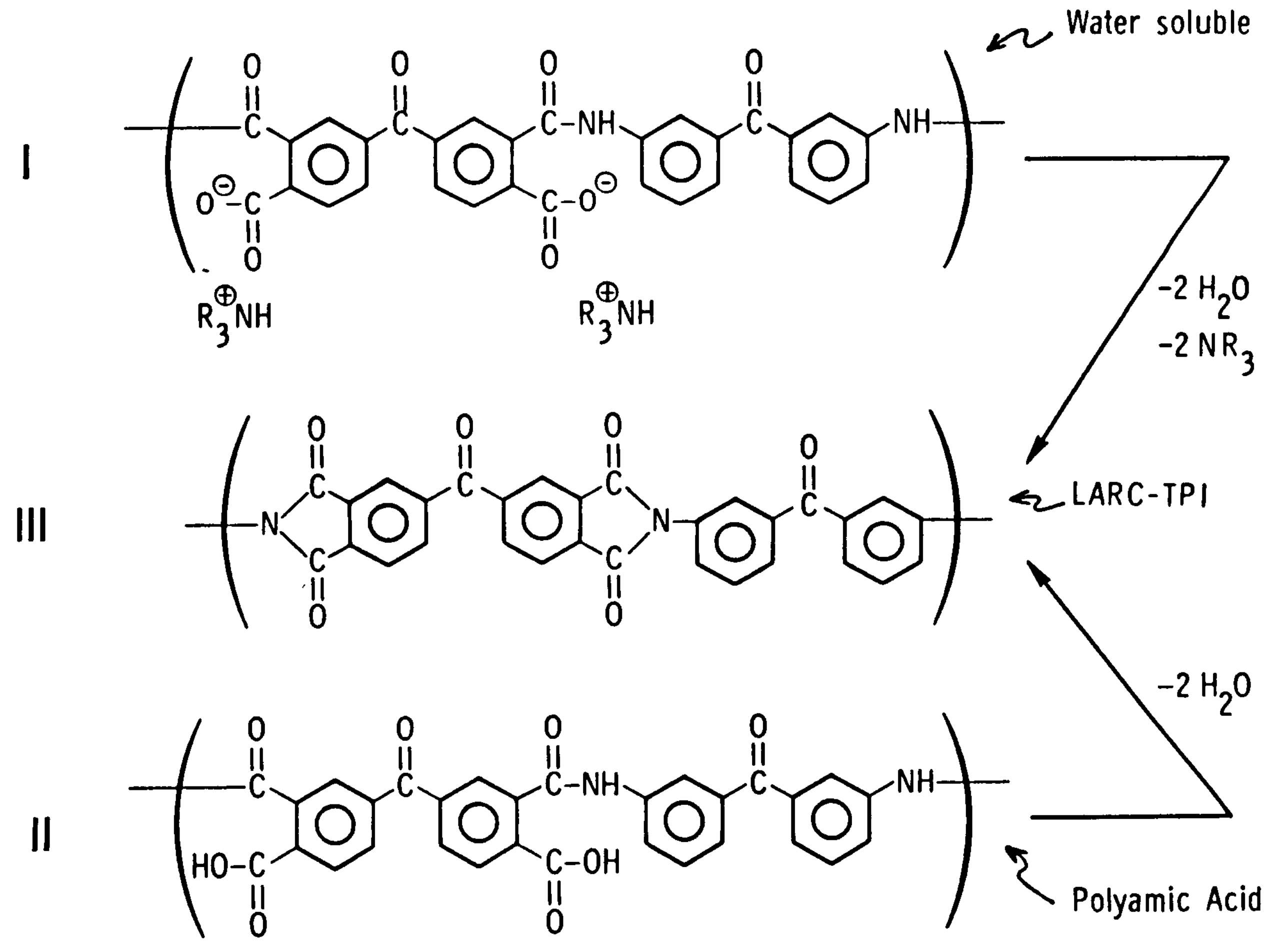

Figure 2. Chemistry for water-soluble version TPI(MTC)/H2O, I, and polyamic-acid version (TPI/MTC), II, which form the polyimide LARC-TPI.

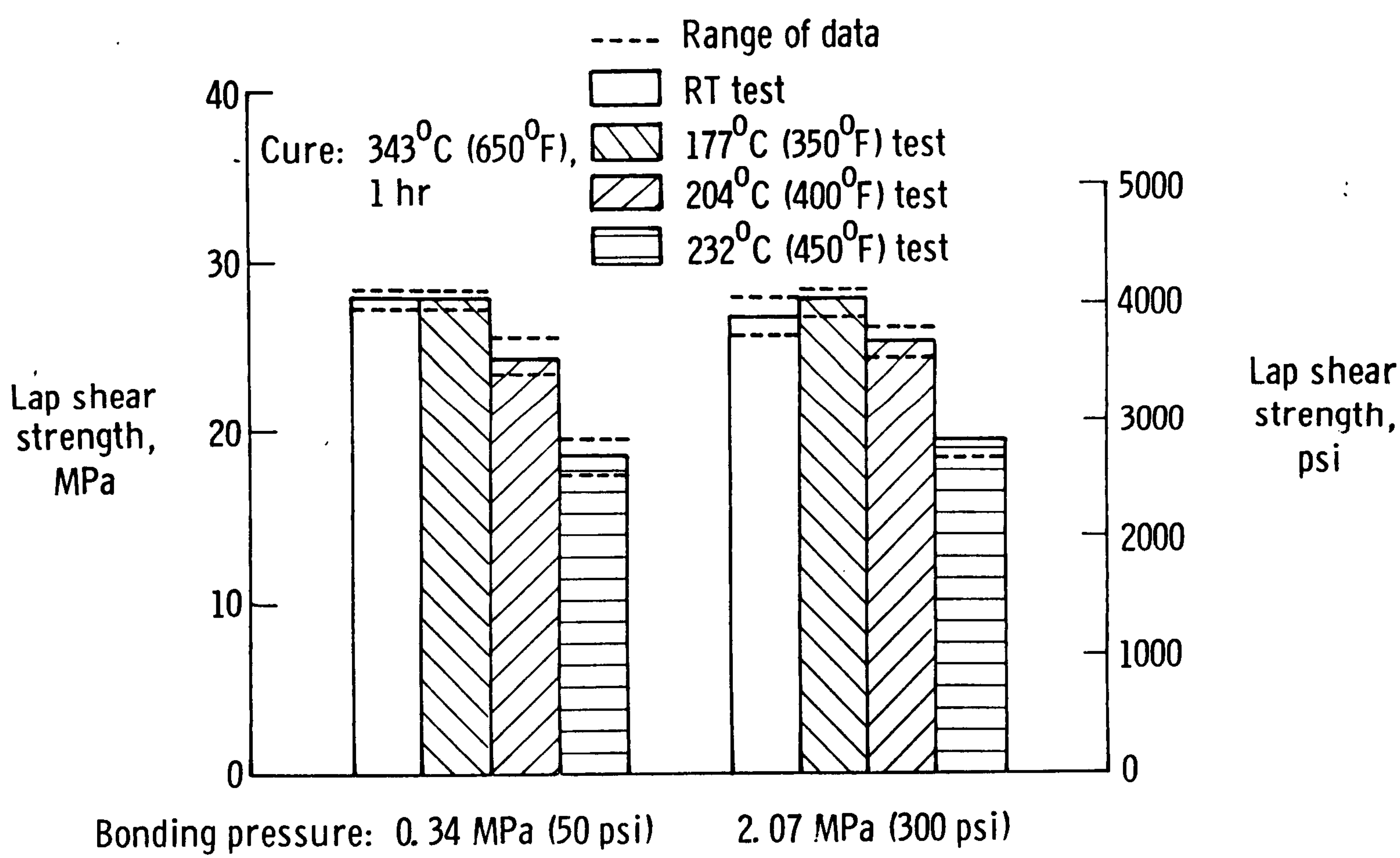

Figure 3. Effect of bonding pressure on lap shear strength for TPI(MTC)/H2O adhesive bonded Ti-6Al-4V.

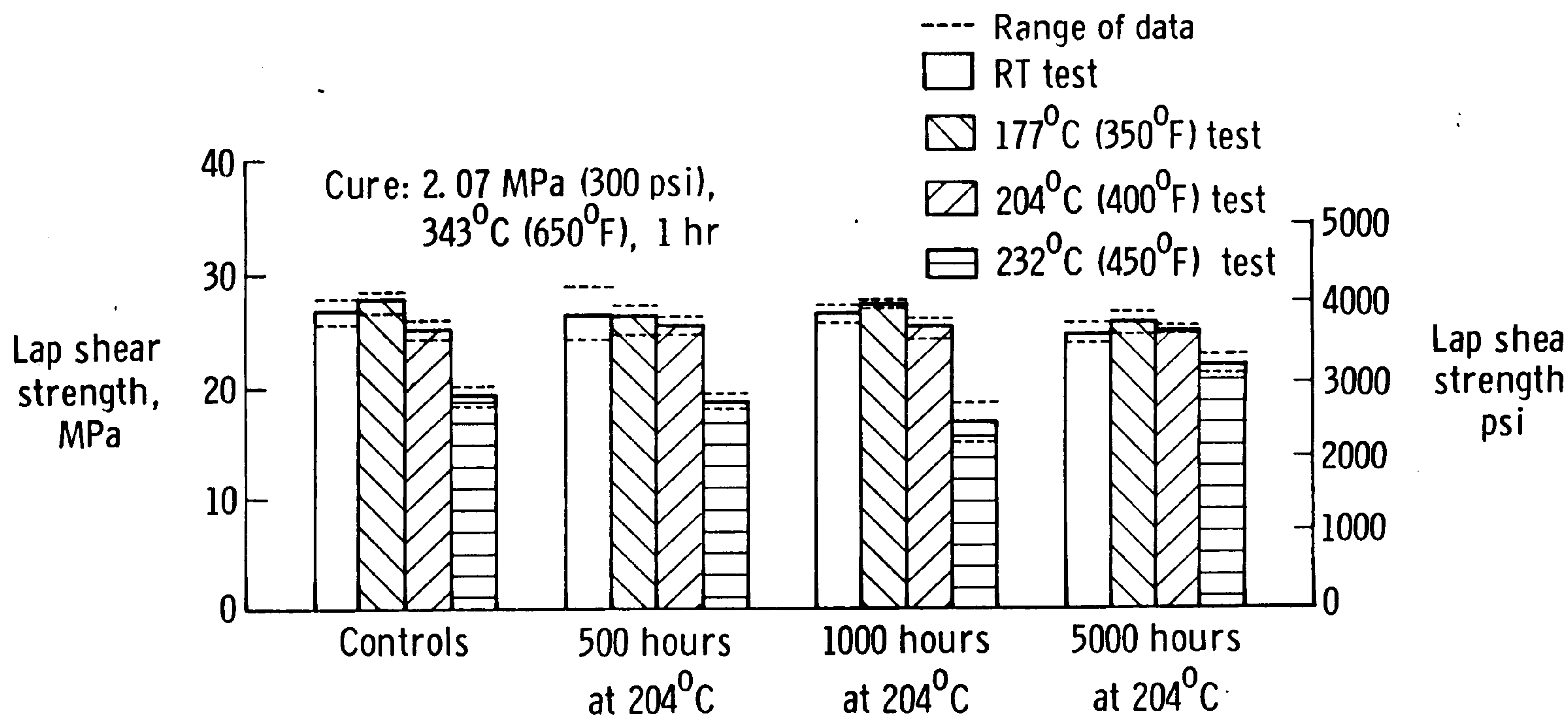

Figure 4. Effect of thermal exposure in air at 204°C (400°F) for TPI(MTC)/H20 adhesive bonded Ti-6Al-4V.

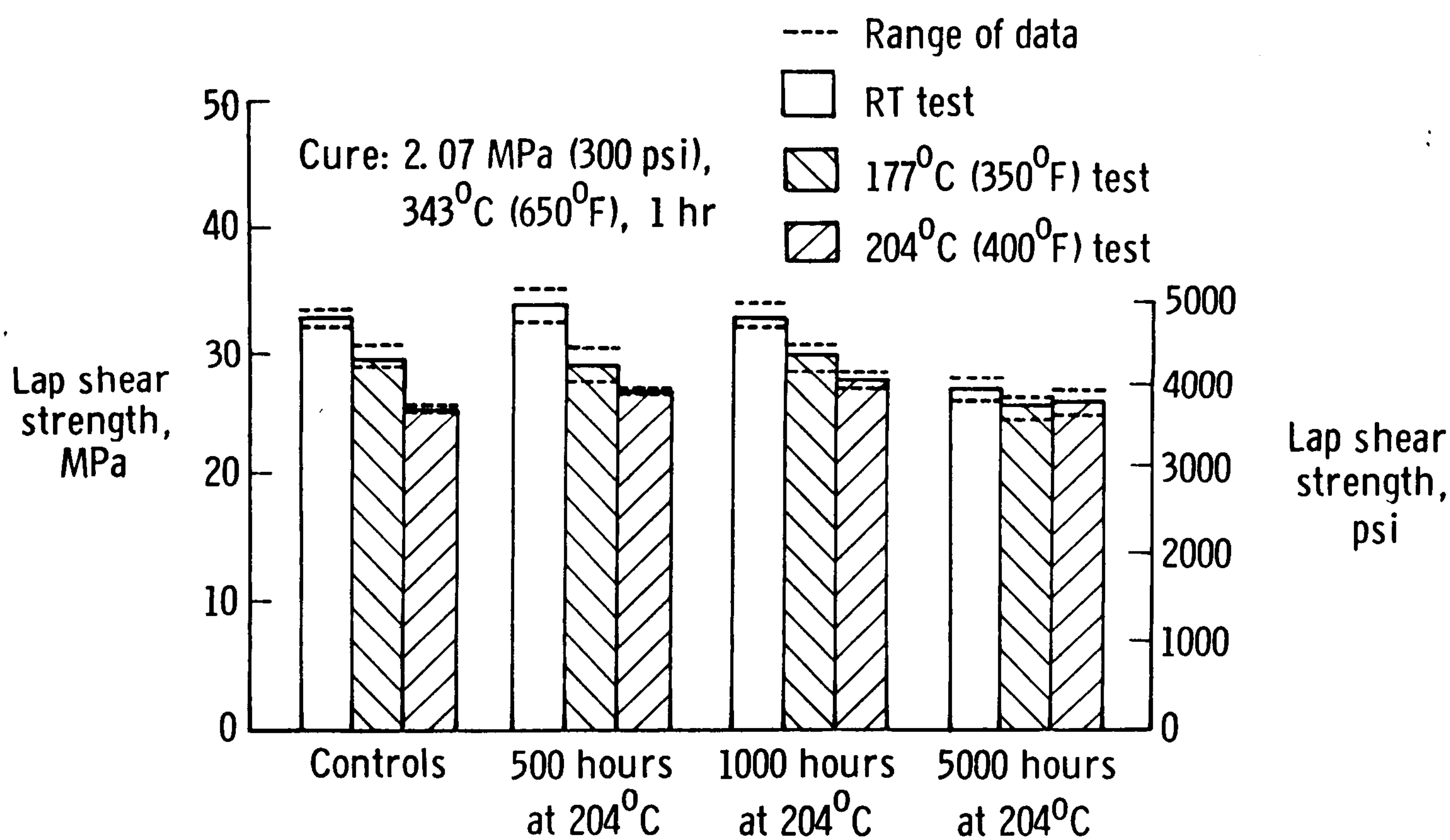

Figure 5. Effect of thermal exposure in air at 204°C (400°F) for TPI/MTC adhesive bonded Ti-6Al-4V.

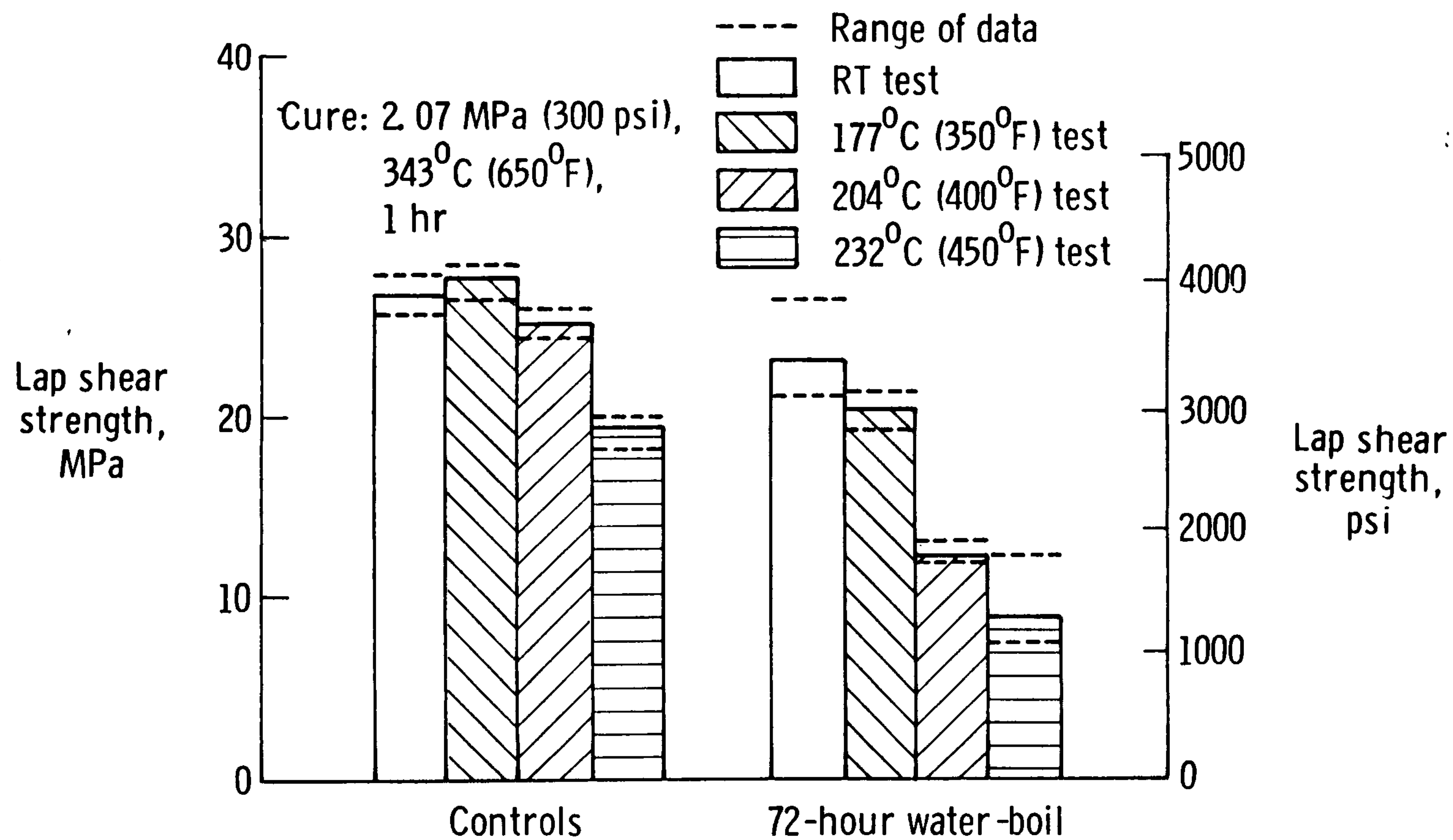

Figure 6. Effect of a 72-hour water-boil on lap shear strength for TPI(MTC)/H2O adhesive bonded Ti-6Al-4V.

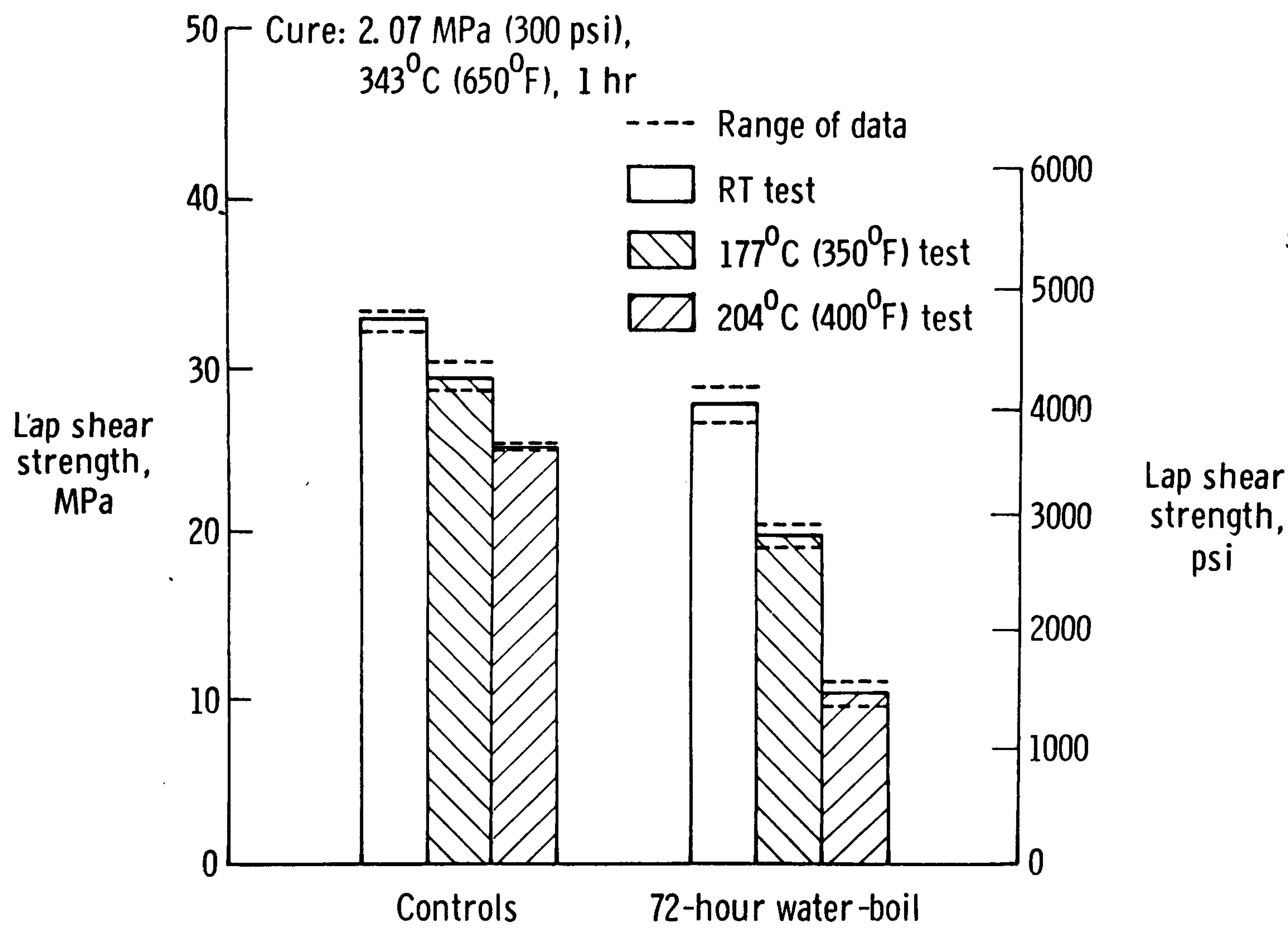

Figure 7. Effect of a 72-hour water-boil on lap shear strength for titanium bonded with TPI/MTC.

Standard Bibliographic Page

1. Report No. NASA TM-89152	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle Adhesive Evaluation of Water-Soluble LARC-TPI		5. Report Date June 1987
		6. Performing Organization Code
7. Author(s) Donald J. Progar and Roscoe A. Pike		8. Performing Organization Report No.
9. Performing Organization Name and Address NASA Langley Research Center Hampton, VA 23665-5225		10. Work Unit No. 505-63-01-01
		11. Contract or Grant No.
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, DC 20546		13. Type of Report and Period Covered Technical Memorandum
		14. Sponsoring Agency Code

15. Supplementary Notes Use of trade names or manufacturers does not constiture an official endorsement, either expressed or implied, by the National Aeronautics and Space Administration. Donald J. Progar, NASA Langley Research Center; Roscoe A. Pike, United Technologies Research Center, East Hartford, CT 06108

16. Abstract

A water-soluble version of the linear thermoplastic polyimide, LARC-TPI, prepared by United Technologies Research Center, East Hartford, Connecticut from the polyamic-acid/diglyme solution commercially marketed by Mitsui Toatsu Chemicals, Incorporated (MTCI), Tokyo, Japan was evaluated as a high temperature thermoplastic adhesive. A water-solvent polyimide system has the advantages of low solvent cost and environmental acceptability due to nontoxicity during manufacture and processing.

This report details the results of a study to evaluate the water-soluble polyimide, identified as TPI(MTC)/H2O, as a high temperature thermoplastic adhesive for bonding Ti-6Al-4V and comparing those results primarily with results reported in earlier work with the polyamic-acid/diglyme material supplied by MTCI.

The lap shear strength test was the primary test performed to evaluate the adhesive before (controls) and after thermal exposure in air at 204°C for up to 5000 hrs and after a 72-hour water-boil exposure. Lap shear strengths were determined at RT, 177°C, 204°C, and 232°C. The adhesive was also characterized after fracture by determining the glass transition temperature as well as defining the mode of failure by visual observation.

In general, the results indicate that the TPI(MTC)/H2O retains high lap shear strengths after thermal exposure but had reduced strengths after the water-boil exposure. All failures were cohesive. The TPI(MTC)/H2O compared very well with previous data reported for the standard polyamic-acid/diglyme LARC-TPI results and, therefore, shows promise as a water-soluble adhesivé for use in various applications.

17. Key Words (Suggested by Authors(s)) Polyimides Thermoplastic Adhesive LARC-TPI Water-Soluble		18. Distribution Statement Unclassified - Unlimited Subject Category 27	
19. Security Classif.(of this report) Unclassified	20. Security Classif.(of this page) Unclassified	21. No. of Pages 28	22. Price A03

For sale by the National Technical Information Service, Springfield, Virginia 22161

NASA Langley Form 63 (June 1985)